

IN THE UNITED STATES PATENT  
AND TRADEMARK OFFICE

In re the application of:

WATANABE et al.

Group Art Unit: 1796

Serial No. 10/586,409

Examiner: Michael L. Leonard

Filed: July 19, 2006

For: LIQUID POLYETHERCARBONATEDIOL COMPOUND AND  
THERMOPLASTIC POLYURETHANE OBTAINED THEREFROM

DECLARATION UNDER RULE 132

Honorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, ATSUSHI MORIKAMI, a citizen of Japan, residing at Ube  
Laboratory, Ube Industries Ltd., 1978-5, Oaza Kogushi,  
Ube-shi, Yamaguchi-ken, Japan, do hereby declare as follows

(1) I graduated from the Graduated School of the  
University of Hiroshima, Master's Course, Department of  
Industrial Chemistry, in March, 1999, and hold a degree of

Master of Engineering from the University of Hiroshima.

(2) Since April 1999, I have been continuously employed by UBE INDUSTRIES, LTD.

(3) Since January, 2002, I have been engaged in research into a production of polyethercarbonatediols and thermoplastic polyurethane resins.

(4) I am a coinventor of the invention of above-captioned U.S. patent Application, presently outstanding, with respect to an liquid polyethercarbonatediol compound and a thermoplastic polyurethane obtained therefrom.

(5) I am thoroughly familiar with the constitution and production of liquid polyethercarbonatediols and thermoplastic polyurethanes, because I have been closely involved, during the past several years, in the evolution of domestic and international patents and patent applications concerning liquid polyethercarbonatediols and thermoplastic polyurethanes.

(6) In the liquid polyethercarbonatediol compound of the present invention comprising a reaction product of (1) a

carbonate ester compound with (2) a polyetherdiol compound having oxyalkylene units, it is essential that the oxyalkylene units of the polyetherdiol compound consist of:

(A) at least one structural unit represented by formula (a):



in which formula (a), R represents a member selected from unsubstituted linear alkylene groups having 3 to 5 carbon atoms and substituted alkylene groups each constituted from a linear alkylene backbone chain having 3 to 5 carbon atoms and at least one alkyl side chain attached to the backbone chain and having 1 to 4 carbon atoms, and

(B) at least one structural unit selected from those represented by the formulae (b) and (c):



and



wherein an average molar number  $n$  of the structural units of the formula (b) and an average molar number of  $m$  of the structural units of the formula (c) each per mole of the structural units of the formula (a) contained in the polyetherdiol compound (2) are, respectively and independently from each other a positive number satisfying the requirements:

$$0 \leq n \leq 5$$

and

$$0 \leq m \leq 5,$$

and the sum  $(n + m)$  of the average molar numbers  $n$  and  $m$  of the structural units of the formulae (b) and (c) is a positive number satisfying the requirement:

$$1 < (n + m) \leq 5.$$

Thus, the polyetherdiol for the polyethercarbonatediol of the present invention is absolutely

free from oxyhexylene units of the formula:



The thermoplastic polyurethane of the present invention is limited to an addition reaction product of the liquid polyethercarbonatediol as defined above with a polyisocyanate compound and with a chain extender.

The specific polyethercarbonatediol as claimed in claim 1 of the present invention enables the resultant thermoplastic polyurethane resin to exhibit a very high ultimate elongation which cannot be unexpected from Tanaka et al.

The unexpected effect of the polyethercarbonatediol of the present invention will be clearly illustrated by the following Experimental Report.

(7) Experimental Report

Experiment 1 (Comparative, Corresponding to Example 5 of Tanaka)

(1) Preparation of a polyether diol compound (I)

A polyethylene diol (1) was prepared by

reacting 1,6-hexanediol ( $\text{HO}-\text{C}_6\text{H}_{12}-\text{OH}$ ) with ethylene oxide ( $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$ ) in a molar ratio of 1:2.03 under a reduced pressure of 411.6 to 266.6 Pa (3.5 to 2.0 mmHg), and the resultant reaction product was distilled at a distillation temperature of 148 to 195°C.

The property of the resultant polyether diol (1) are shown in Table 1.

(2) Production of a liquid polyethercarbonate diol (1)

A glass reactor equipped with a stirrer, a thermometer and a distillation column (having a fractional distillation pipe, a refluxing head and a condenser equipped on the top portion thereof), and having a capacity (inner volume) of one liter was charged with 2.30 mole of the polyether diol (1), 2.06 mole of dimethyl carbonate, and 0.507 mmol of a catalyst consisting of tetra-n-butoxytitanium. The resultant reaction mixture was heated to a temperature of 170°C and kept at this temperature for 2 hours under reflux. Then, the reaction mixture was gradually heated to a temperature of 190°C over a time of 6.5 hours, while a mixture of a by-product consisting of

methyl alcohol with non-reacted dimethyl carbonate is distilled off, and was kept at the temperature of 190°C under a reduced pressure of 13332.2 Pa (100 mmHg) for 3 hours while the mixture of methyl alcohol and dimethyl carbonate is distilled off. Further, the resultant reaction mixture was subjected to the reaction at a temperature of 190°C under a pressure of 693.3 to 93.3 Pa (5.2 to 0.7 mmHg) for 9 hours, while the non-reacted polyether diol (1) was distilled off. A liquid polyethercarbonate diol having a hydroxyl value of 49.8 mg KOH/g was obtained.

The resultant liquid polyethercarbonate diol was mixed with 0.024 mol of the polyether diol (1), and the resultant mixture was stirred at a temperature of 185°C under a pressure of 26664.4 Pa (200 mmHg) for 2 hours, to control the molecular weight of the polyethercarbonate diol. The resultant liquid polyethercarbonate diol was mixed with dibutyl phosphate in a molar amount equal to that of the above-mentioned catalyst, the mixture was stirred at a temperature of 130°C under a pressure of 13332.2 Pa (100 mmHg) for 2 hours, to inactivate the catalyst. The properties of the resultant liquid polyethercarbonate diol (1) are shown in Table 1.

(3) Production of thermoplastic polyurethane (1)

In a glass reactor having a capacity (inner volume) of one liter and equipped with a stirrer, a thermometer and a cooling pipe, 60g (0.0295 mol) of the liquid polyethercarbonate diol (A) and 5.33g (0.0592 mol) of 1,4-butanediol were completely dissolved in 204g of dimethylformamide at a temperature of 60°C.

Then, into the solution, 4,4'-diphenylmethane diisocyanate was mixed in an amount of 24.37g (0.0974 mol) and the mixture was heated at a temperature of 80°C for 2 hours, to produce a thermoplastic polyurethane resin (1).

The resultant solution of the thermoplastic polyurethane (1) was heated to a temperature of 60°C, cast on a releasing glass plate, and heat-treated at a temperature of 70°C for one hour and then at 120°C for 2 hours. A thermoplastic polyurethane film having a thickness of about 200  $\mu\text{m}$  was obtained. The properties of the film are shown in Table 2.



Experiment 2 (Comparative, Corresponding to  
Example 8 of Tanaka)

(1) Preparation of polyether diol (2)

A polyether diol (2) was prepared by reacting 1,6 hexanediol with ethylene oxide in a molar ratio of 1:1.04, and distilling the resultant reaction product under a reduced pressure of 533.3 to 66.7 Pa (4.0 to 0.5 mmHg) at a distillation temperature of 150 to 185°C. The property of the resultant polyether diol (2) are shown in Table 1.

(2) Production of a Liquid Polyethercarbonate  
Diol (2)

The same glass reactor as in Experiment 1 was charged with 2.30 mole of the polyether diol (2), 2.51 mole of dimethyl carbonate, and 0.232 mmol of a catalyst consisting of tetra-n-butoxytitanium. The resultant reaction mixture was heated to a temperature of 160°C and kept at this temperature for 2 hours under reflux. Then, the reaction mixture was gradually heated to a temperature of 190°C over a time of 6.5 hours, while a mixture of methyl alcohol with non-reacted dimethyl carbonate is distilled off, and was kept at a temperature of 190°C under a reduced pressure of 39996.6 Pa (300 mmHg) for 0.5 hours and then under a pressure

of 13332.2 Pa (100 mmHg) for 3 hours while the mixture of methyl alcohol and dimethyl carbonate was distilled off. Further, the resultant reaction mixture was subjected to the reaction at a temperature of 190°C under a pressure of 253.3 to 26.7 Pa (1.9 to 0.2 mmHg) for 4.5 hours, while the non-reacted polyether diol (2) is distilled off.

The resultant liquid polyethercarbonate diol was mixed with 0.023 mol of the polyether diol (2), and the resultant mixture was treated in the same manner as in Experiment 1 to control the molecular weight of the polyethercarbonate diol. The resultant liquid polyethercarbonate diol was treated in the same manner as in Experiment 1, to inactivate the catalyst. The properties of the resultant liquid polyethercarbonate diol (2) are shown in Table 1.

### (3) Production of thermoplastic polyurethane (2)

In the same glass reactor as in Experiment 1, 50g (0.0251 mol) of the liquid polyethercarbonate diol (2) and 12.3g (0.0491 mol) of 4,4'-diphenylmethane diisocyanate were completely dissolved in 148g of dimethylformamide at a temperature of 60°C.

The solution was subjected to a reaction procedure at a temperature of 80°C for 2 hours. Then, the resultant solution was mixed with 3.08g (0.0503 mol) of 2-ethanolamine (EA, chain extender) and 20g of dimethylformamide, and the resultant solution was subjected to a reaction procedure at room temperature for 1.45 hours to prepare a prepolymer having hydroxyl groups located in the two terminals of each prepolymer molecule.

Into the prepolymer solution, 4,4'-diphenylmethane diisocyanate (DI) was mixed in an amount of 7.74g (0.0310 mol). The resultant reaction solution was left to stand at room temperature for 20 minutes and then was subjected to the same reaction procedures as in Experiment 1.

The molar ratio of the polyethercarbonate diol (2), the chain extender (EA) and 4,4'-diphenylmethane diisocyanate to each other was 1:2:3.

The resultant solution of the thermoplastic polyurethane (2) was formed into a film by the same procedures as in Experiment 1. A thermoplastic polyurethane

film having a thickness of about 200  $\mu\text{m}$  was obtained. The properties of the film are shown in Table 2.

Experiment 3 (Comparative, Corresponding to  
Example 10 of Tanaka)

Preparation of thermoplastic polyurethane (3)

In the same glass reactor as in Experiment 1, 50g (0.0251 mol) of the liquid polyethercarbonate diol (2) and 2.57g (0.0503 mol) of 4,4'-diphenylmethane diisocyanate were completely dissolved in 139g of dimethylformamide at a temperature of 60°C.

The solution was subjected to a reaction procedure at a temperature of 80°C for 2 hours. Then, the resultant solution was mixed with 1.53g (0.0251 mol) of 2-ethanolamine and 20g of dimethylformamide, and the resultant solution was subjected to a reaction procedure at room temperature for 2.1 hours to prepare a prepolymer having hydroxyl groups located in the two terminals of each prepolymer molecule.

The resultant prepolymer solution was left to stand at room temperature for 20 minutes and then was subjected to the same reaction procedures as in Experiment 1.

The reaction was stopped at a stage at which substantially no increase in viscosity of the solution was detected, namely 10 hours after the start of the reaction.

The properties of the polyetherdiol (3) and the polyethercarbonatediol (3) are shown in Table 1.

The resultant solution of the thermoplastic polyurethane (3) was formed into a film by the same procedures as in Experiment 1. A thermoplastic polyurethane film having a thickness of about 200  $\mu\text{m}$  was obtained. The properties of the film are shown in Table 2.

#### Experiment 4 (Comparative)

The same procedures as in Experiment 3 was carried out, except that in the preparation of polyetherdiol (4), 1,6-hexanediol was replaced by a mixture of 1,6-hexanediol with 1,5-pentanediol in a molar ratio of 6/4, to provide a polyetherdiol (4), then a liquid polyethercarbonate diol (4) and then a thermoplastic polyurethane (4).

The properties of polyetherdiol (4) are shown in

Table 1.

The properties of the liquid polyethercarbonate diol (4) are shown in Table 1.

The properties of the thermoplastic polyurethane (4) are shown in Table 2.

Experiment 5 (The present invention)

The results of Experiments 1 to 4 were compared with the results of Experiment 5 which is identical to Example 5 of the present application, as follows.

(1) Preparation of polyether diol (5)

A polyether diol (5) was prepared by an addition reaction of 1,5-pentandiol with ethyleneoxide in a molar ratio of 1:1.02, and the resultant reaction product was distilled under the same conditions as in Experiment 1.

The properties of the resultant polyether diol (V) are shown in Table 1.

Production of a liquid polyethercarbonate diol (5)

A liquid polyethercarbonate diol (4) was produced by the same procedure as in Experiment 2, except that the polyether diol (2) was replaced by 2.30 moles of the polyether diol (5).

The resultant liquid polyethercarbonate diol was mixed with 3.68g (0.023 moles) of polyetherdiol (5) to control the molecular weight of the liquid polyethercarbonate diol in the same manner as in Experiment. The properties of the liquid polyethercarbonate diol (5) are shown in Table 1.

#### Production of thermoplastic polyurethane (5)

In the same reactor as used in Experiment 1, 50g (0.0254 mole) of the liquid polyethercarbonatediol (5) and 12.70g (0.0508 mole) of 4,4'-diphenylmethane diisocyanate were completely dissolved in 130g of dimethylformamide at a temperature of 60°C. The resultant solution was subjected to a reaction at a temperature of 80°C for 2 hours. The properties of the resultant thermoplastic polyurethane (5) film are shown in Table 2.

#### RESULTS

Table 1 Composition of Polyether diols and Properties of Polyethercarbonate diols

	Polyether diol	Polyethercarbonate diol		
	Molar ratio of two types of units to one another	Mn	Tg (°C)	Viscosity (Pa·s)
1 (Comparative)	(a) / (b) = 2.03	2034	-58.1	0.620
2 (Comparative)	(a) / (b) = 1.04	1991	-61.1	0.906
3 (Comparative)	(a) / (b) = 1.04	1991	-61.1	0.906
4 (Comparative)	[(a) + (d)] / (b) = 1.04	1982	-59.6	0.702
5 (The present invention)	(d) / (b) = 1.02	1968	-54.7	0.552

[Note]

(a):  $-(\text{CH}_2)_6\text{O}-$

(b):  $-(\text{CH}_2)_2\text{O}-$

(d):  $-(\text{CH}_2)_5\text{O}-$

Mn: Number average molecular weight



Table 2 Composition and Properties of Thermoplastic polyurethane resins

Experiment No.	Isocyanate	Type and molar ratio of chain extender to PECD	Thermoplastic polyurethane resin film							Hysteresis loss (%)
			T <sub>g</sub> (°C)	Initial modulus (MPa)	100% elongation (MPa)	200% elongation (MPa)	300% elongation (MPa)	Tensile Strength (MPa)	Ultimate elongation (%)	Permanent set (%)
1 (Comparative)	3	BD/2	-25	9.5	3.7	5.5	8.1	35.4	567	14
2 (Comparative)	3	EA/2	-27	7.8	6.3	11.6	21	59.7	447	7.5
3 (Comparative)	2	EA/1	-27	3.4	2.2	3.2	4.6	29.1	640	12
4 (Comparative)	2	EA/1	-29	3.3	1.8	2.6	3.7	23.5	578	13
5 (The present invention)	2	EA/1	-32	3.0	1.1	1.8	2.4	15.1	892	15.0
										77

Note MDI: Molar ratio of diisocyanate/polyethercarbonate diol (PECD)

BD: 1,4-butanediol

EA: 2-ethanolamine

## DISCUSSION

In Experiment 1 (comparative), a thermoplastic polyurethane resin was prepared in accordance with Example 5 of US 2002/0123595 A1, Tanaka et al. In the first step, a polyether diol (1) was prepared from 1,6-hexane diol and ethylene oxide in a molar ratio of 1:2.03. In the second step, a liquid polyethercarboxylate diol (1) was prepared from the polyether diol (1) and dimethyl carbonate in a solar ratio of 2.30/2.06 in the presence of a catalyst. The resultant liquid polyethercarboxylate diol (1) had the properties as shown in Table 1.

In the third step, a thermoplastic polyurethane resin (1) was prepared from the liquid polyethercarbonate diol (1), 1,4-butane diol (BD, a chain extender) and 4,4'-diphenylmethane diisocyanate (DI) in a molar ratio of 1:2:3.

The resultant thermoplastic polyurethane resin (1) exhibited an ultimate elongation of 567% which was unsatisfactorily low.

In Experiment 2 (comparative), the polyether diol (2) was prepared from 1,6-hexanediol and ethylene oxide in a molar ratio of 1:1.04, and the liquid polyethercarbonate

diol (2) was prepared from polyetherdiol (2) and dimethyl carbonate in a molar ratio of 2.30:2.51, in the presence of a catalyst.

In the production of the thermoplastic polyurethane resin (2), the chain extender consisted of 2-ethanolamine in place of 1,4-butanediol used in Experiment 1, and the molar ratio of the liquid polyethercarbonate diol, the chain extender (EA) and 4,4'-diphenylmethane diisocyanate to each other was 1:2:3. As a result, the thermoplastic polyurethane resin (2) exhibited an ultimate elongation of 447% which was lower than that of Experiment 1 and thus unsatisfactory.

In Experiment 3 (comparative), the procedures of Experiment 2 were changed as follows.

The same liquid polyethercarbonate diol (2) as in Experiment 2 was reacted with 2-ethanol amine and 4,4'-diphenylmethane diisocyanate in a molar ratio of 1:1:2 for the purpose of obtaining a thermoplastic polyurethane resin having an increased ultimate elongation.

The resultant thermoplastic polyurethane resin (3) exhibited an ultimate elongation of 640% which was higher

than that of Experiments 1 and 2, but still not satisfactory.

In Experiment 4 (comparative), the same procedures of Experiment 3 were repeated with the following exception.

In the preparation of the polyester diol (4), a mixture of 1,6-hexanediol with 1,5-pentanediol in a molar ratio of 0.6:0.4 was employed in place of 1,6-hexanediol with reference to the statement such that in the preparation of the polyether diol, optionally, a portion (preferably 50 molar% or less) of 1,6-hexanediol is replaced by one or more diol compound, in passage [0039] of Tanaka et al., and the molar ratio of the mixture of 1,6-hexanediol with 1,5-pentanediol to ethylene oxide was 1.04.

The resultant thermoplastic polyurethane resin (4) exhibited an ultimate elongation of 678% which was higher than that of Experiments 1, 2 and 3, but still not satisfactory.

In Experiment 5 (the present invention), the procedures of Experiment 3 were modified in that the polyether diol was prepared from 1,5-pentanediol (in place of 1,6-hexanediol) and ethylene oxide in a molar ratio of 1.02:1. The resultant

thermoplastic polyurethane resin (5) exhibited a satisfactorily high ultimate elongation of 892%.

#### Conclusion

In view of the results of Experiments 1 to 5, it is true that the use of the polyetherdiol having the specific oxyalkylene units as defined in claim 1 causes the resultant thermoplastic polyurethane resin to exhibit an unexpectedly high ultimate elongation, in comparison with the polyurethane resins disclosed in US 2002/0123595 A, Tanaka et al.

Thus, Tanaka et al. do not hinder the patentability of the polyethercarbonate diol and the polyurethane resin of the present invention.

The undersigned declarant declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 1st day of April, 2010.

Atsushi Morikami

Atsushi Morikami